Suppression of magnetism in Ba_{5}AlIr_{2}O_{11}: Interplay of Hund's coupling, molecular orbitals, and spin-orbit interaction

Sergey V. Streltsov, Gang Cao, and Daniel I. Khomskii

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Suppression of magnetism in $Ba_5AlIr_2O_{11}$: interplay of Hund's coupling, molecular orbitals and spin-orbit interaction

Sergey V. Streltsov,[1,2] Gang Cao,[3] and Daniel I. Khomskii[4]

[1] *Institute of Metal Physics, S. Kovalevskoy St. 18, 620990 Ekaterinburg Russia*
[2] *Ural Federal University, Mira St. 19, 620002 Ekaterinburg, Russia**
[3] *Center for Advanced Materials, Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506, USA*
[4] *II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln, Germany*

The electronic and magnetic properties of $Ba_5AlIr_2O_{11}$ containing Ir-Ir dimers are investigated using the GGA and GGA+SOC calculations. We found that strong suppression of the magnetic moment in this compound recently found in [J. Terzic *et al.*, Phys. Rev. B **91**, 235147 (2015)] is not due to charge-ordering, but is related to the joint effect of the spin-orbit interaction and strong covalency, resulting in the formation of metal-metal bonds. They conspire and act against the intra-atomic Hund's rule exchange interaction to reduce total magnetic moment of the dimer. We argue that the same mechanism could be relevant for other $4d$ and $5d$ dimerized transition metal compounds.

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Introduction.– The study of $4d$ and especially $5d$ transition metal compounds, in particular those of Ir, is now at the forefront of research in the physics of correated electron systems. This is largely connected with novel effects caused by strong spin-orbit coupling (SOC). In particular, for Ir^{4+} with t_{2g}^5 electronic configuration, with spin $S = 1/2$ and effective orbital moment $L_{eff} = 1$, strong SOC can stabilise for an isolated ion the state with $J = 1/2$, which can explain Mott insulating character of Sr_2IrO_4[1] or could lead for honeycomb systems Li_2IrO_3 and Na_2IrO_3 to special states like those described by Kitaev model[2] (see also Ref.[3]). But no less interesting could be possible nontrivial properties of systems with Ir^{5+} and Ru^{4+}, with ionic configuration t_{2g}^4 ($S = 1$, $L_{eff} = 1$), which in case of isolated ions are in nonmagnetic $J = 0$ state[4]. And indeed for ESR (electron spin resonance) community Ir^{5+} is a classical nonmagnetic ion, even sometimes used for nonmagnetic dilution. However, in concentrated solids the intersite interaction, if strong enough, can in principle lead to magnetic ordering in such systems – the phenomenon known as singlet magnetism, see e.g. Ch. 5.5 in Ref.[5] and Ref.[6]. Apparently such magnetic state was discovered in double perovskite Sr_2YIrO_6 in Ref.[7], although the properties of this and similar systems is still a matter of debate[8].

An interesting system $Ba_5AlIr_2O_{11}$[9] was recently experimentally studied in details in Ref.[10]. The main building blocks of it are dimers of face-sharing IrO_6 octahedra with, on the average, mixed valence $Ir^{4.5+}$, which may be expected to combine both the properties typical for Ir^{4+} and for Ir^{5+}. However in contrast to the single-site physics (leading to $J = 1/2$ state for Ir^{4+} and $J = 0$ for Ir^{5+} ions) here we deal with strongly coupled pair of Ir ions, in which, for example, intersite electron hopping can easily be of order or even larger than the intra-atomic parameters such as the Hund's rule coupling J_H and spin-orbit coupling λ, and can compete with the intra-atomic Hubbard repulsion U. Indeed, in going from $3d$ to $4d$ and $5d$ ions, U decreases, from $\sim$5 eV for $3d$ to $2-3$ eV for $4d$ and to $1-2$ eV for $5d$. Similarly, $J_H \sim 0.7-0.9$ eV for $3d$, $0.5-0.6$ for $4d$, and ~ 0.5 eV for $5d$ systems[11]. At the same time the size of $d-$orbitals, and with it the $pd-$ and $dd-$hoppings increase in this series, and can easily reach $1-1.5$ eV for $4d-5d$ systems[12–14]. In this situation there may occur strong modification of the behaviour expected for isolated $5d$ (e.g. Ir) ions. $Ba_5AlIr_2O_{11}$ may be a good example on which one can investigate relative importance of single-site vs intersite effects.

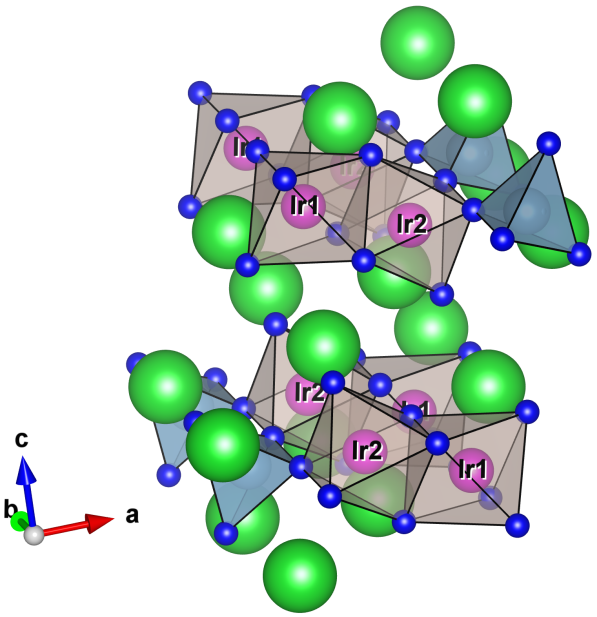

FIG. 1: (color online). Crystal structure of $Ba_5AlIr_2O_{11}$. Ir ions (violet balls) are in the oxygen (small blue balls) octahedra. Two nearest IrO_6 octahedra form dimer, sharing their faces. Al (large blue balls) ions are in the oxygen tetrahedra and Ba (green balls) sits in the voids.

The crystal structure of $Ba_5AlIr_2O_{11}$ consists of Ir-Ir dimers, which form chains, as shown in Fig. 1. At T_S = 210 K there occurs a structural phase transition accompanied by the metal-insulator transition[10]. While even at room temperature there is a certain difference in the average Ir-O distance for two classes of Ir (Ir2 occupies octahedra, which share their corners with AlO_4 tetrahedra; Ir1 is in the center of the remaining octahedra), it increases at T_S. Thus, one could speak about certain charge ordering even for $T>T_S$, if this high temperature phase was insulating. The real charge disproportionation in limiting case $2Ir^{4.5+} \rightarrow Ir^{4+}+Ir^{5+}$, seems to occur only in the insulating phase below T_S as manifested by a strong dielectric anomaly at T_S and by increasing difference in the average Ir-O bond distance for two classes of Ir.[10]

Below T_M=4.5 K there appears a long range magnetic order in $Ba_5AlIr_2O_{11}$ apparently an antiferromagnetic one, consistent with negative Curie-Weiss temperature ($\theta = -14$ K). The effective magnetic moment, obtained by the high temperature fit of susceptibility is $\mu_{eff} = 1.04\mu_B$/dimer, much smaller than one would expect from the values of spin moments corresponding to Ir^{4+} ($\mu_s = 1\mu_B$/Ir) or Ir^{5+} ($\mu_s = 2\mu_B$/Ir)[10]. The mechanism of such a strong suppression was proposed in Ref.[10]. It was argued that it is related to the joint effect of the strong spin-orbit coupling and formation of singlet molecular orbitals for part of Ir 5*d* orbitals.

In this paper we theoretically investigate this problem using *ab initio* band structure calculations. We demonstrate that indeed in this material, as possibly also in other 5*d* compounds, there exist strong interplay of covalent bond formation, Hund's rule coupling and spin-orbit interaction, which results in particular in strong suppression of magnetic moment on Ir ions and which strongly modifies intradimer exchange interaction. These results give good explanation of unusual properties of $Ba_5AlIr_2O_{11}$, and show general trend expected in similar materials with competing intrasite and intersite effects.

Ionic treatment.– Before presenting the results of the real band structure calculations, we discuss what one might expect in this system starting from the ionic consideration. Since the $t_{2g}-e_g^\sigma$ crystal-filed splitting is huge for 4*d* and especially 5*d* transition metal oxides, first we have to fill t_{2g} orbitals. Two neighbouring IrO_6 octahedra form dimer sharing their faces. In such geometry there will be two different by symmetry sets of orbitals: a_{1g} orbitals pointing to each other will have stronger hopping, t_a, than e_g^π orbitals, t_e, see Fig. 2(a)[15]. Having nine $5d-$electrons per Ir-Ir dimer one may fill these orbitals in two different ways: to have maximum ($S_{tot} = 3/2$) and minimum ($S_{tot} = 1/2$) total spins, Fig. 2(b) and (c) respectively.

The first configuration with $S_{tot} = 3/2$ can be called double exchange (DE) state, since the electron (hole) on delocalized a_{1g} antibonding orbital with the largest hopping t_a moves from one site to another in the dimer and makes other two electrons (holes) to have the same spin projection. In the second, state with $S_{tot} = 1/2$ the antibonding a_{1g} orbital stays unoccupied and the total magnetic moment is suppressed. One may call this state an orbital-selective (OS) state[16], since e_g^π and a_{1g} orbitals behave very differently in this state.

One may consider this situation within two site - two orbitals (a_{1g} - orbital 1 and e_g^π - orbital 2) model in the simplest ionic approximation taking into account intra-atomic Hund's rule coupling:

$$H_{Hund} = -\sum_{i,mm'} J_H(\frac{1}{2} + 2\vec{S}_{im}\vec{S}_{im'}), \qquad (1)$$

(here i numerates sites in a dimer, $i = \{a, b\}$, m and m' are orbital indexes $m, m' = \{1, 2\}$; the sum runs once over each pair of m and m'), and the kinetic energy, given by hopping parameters between the a_{1g} and e_g^π orbitals, t_a and t_e respectively. With our definition of Hund's exchange, (1), in the mean-field the Hund's energy is equal to $J_H\times$ (number of parallel spins).

The total energy of the DE state, with two localized electrons (on orbital 1 and sites a and b, i.e. $|c^\dagger_{a,1}\rangle$ and $|c^\dagger_{b,1}\rangle$), and a "delocalized" electron on a bonding orbital $|(c^\dagger_{a,2} + c^\dagger_{b,2})/\sqrt{2}\rangle$, all with the same spins and with the total spin of a dimer $S_{tot} = 3/2$, we got the energy of this bonding state with one electron $-t_a$, and the Hund's energy $-J_H/2$ per site. Taking account the fact that "localized" e_g^π electrons still can hop with amplitude $-2t_e$ we find that the total energy of this DE state is $E_{DE} = -t_a - 2t_e - J_H$.

On the other hand, the energy of an OS state with two electrons in a singlet state on bonding orbital, $|(c^\dagger_{a,2\uparrow} + c^\dagger_{b,2\uparrow})(c^\dagger_{a,2\downarrow} + c^\dagger_{b,2\downarrow})/2\rangle$, and with the remaining localized electron on any of the sites, e.g. at a site a with spin $\uparrow$, we got the bonding energy of "itinerant" electrons $-2t_a$, and the reduced Hunds energy $J_H/2$. Thus, $E_{OS} = -2t_a - t_e - J_H/2$. In effect the DE will be realized, if

$$J_H > 2(t_a - t_e) = 2\Delta_{ae}. \qquad (2)$$

The Hund's rule exchange for Ir is ~0.5-0.7 eV[17,18], while both hopping parameters can be found from real *ab initio* calculation. If Δ_{ae} would be large enough, one could explain experimentally observed suppression of magnetic moment only by the covalency, i.e. by formation of metal-metal bonds.

Calculation details.– We used full-potential Wien2k code[19] and generalized gradient approximation (GGA)[20]. The atomic sphere radii were set as following: R_{Ir}=1.91 a.u., R_{Ba}=2.35 a.u., R_{Al}=1.63 a.u., and R_O=1.63 a.u. The spin-orbit coupling (SOC) was treated in a second variational way. 160 k-points were used for the Brillouin-zone integration. The parameter of the plane-wave expansion was chosen to be $R_{MT}K_{max} = 7$, where R_{MT} is the smallest atomic sphere radii and K_{max} - plane wave cut-off. The calculations were performed for the crystal structure obtained by X-ray diffraction at T=90 K[10].

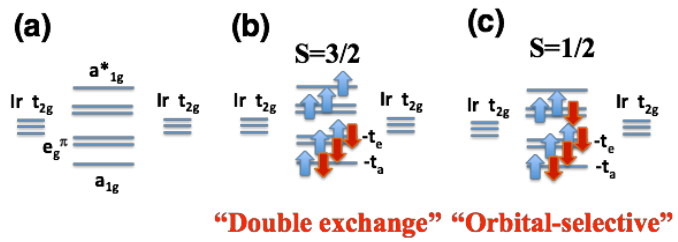

FIG. 2: (color online). The sketch, which shows (a) the level splitting in the dimer constructed out of face-sharing octahedra: the largest bonding-antibonding splitting corresponds to a_{1g} orbitals, directed to each other in this geometry. (b) and (c) illustrates two possible states in such a system with different values of total spin.

Calculation results.– Our nonmagnetic GGA calculation for low-temperature phase indeed indicates a sizeable bonding-antibonding splitting (see lower panel Fig. 3), which is natural for IrO_6 octahedra forming dimers. As we have seen above, the key parameter, which defines the ground state electronic configuration is the splitting between antibonding a_{1g} and e_g^π orbitals, Δ_{ae}. Using the linearized muffin-tin orbitals method[21], the local density approximation and Wannier projection technique[22] we estimated, that Δ_{ae} ∼0.2 eV. In contrast to our expectations, this value is smaller than $J_H/2$. Therefore in contrast to experimental finding[10] according to Eq. (2) the DE, not OS state with small magnetic moment should win in this case.

Indeed, in the magnetic GGA calculations the total spin moment is ∼2.0 μ_B/dimer (smaller than the ionic value due to hybridization effects[23]), while $|\mu_S(\mathrm{Ir1})|$=0.9 μ_B and $|\mu_S(\mathrm{Ir2})|$=0.6 μ_B. It is remarkable that the spin moments on the two Ir ions forming dimers are ferromagnetically coupled (antiferromagnetic solution does not converge in the GGA). Therefore, the exchange coupling between these ions without SOC is governed by the DE. Furthermore, there is an unusually large moment ∼0.5 μ_B/dimer in the interstitial space between the atomic spheres related to the formation of the bonding state, favoring bond-centered spin densities. Thus we see that the covalency alone (the formation of bonding and antibonding states in Ir dimers) is in this system not sufficient to suppress DE and strongly reduce magnetic moment. As we show below, the situation changes drastically when we take into account spin-orbit interaction.

Before presenting these results, we note that there is significant difference between two inequivalent mean Ir-O distances for the two face-sharing octahedra: δ=d[Ir2-O]-d[Ir1-O]=0.016 Å (recalculated from experimental structure in low-temperature phase[10]), compared to δ ∼ 0.055 Å for a full Ir^{4+}/Ir^{5+} charge order[24]. The Bader analysis[25] shows that corresponding charge disproportionation is $\delta n_{Ir1/Ir2}$ ∼ 0.3 electrons (Ir1 is closer to Ir^{5+} and Ir2 to Ir^{4+}), indicating the existence of a charge order.

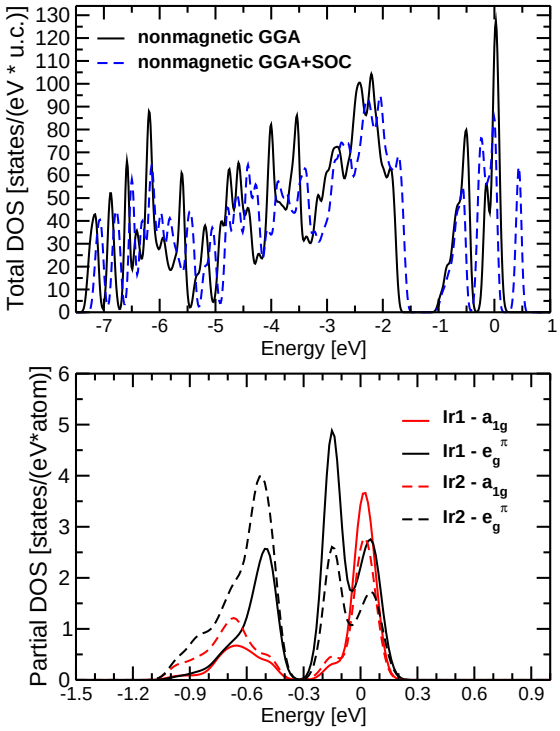

FIG. 3: (color online). Upper panel: total DOS in the nonmagnetic GGA and GGA+SOC calculations. Lower panel: partial DOS in the nonmagnetic GGA in the local coordinate system (LCS), when z axis looks along the vector connecting two Ir in the dimer. This choice of LCS is not ideal, since the symmetry is very low and octahedra are strongly distorted, but one may see that the rightmost peak mostly corresponds to the antibonding a_{1g} orbital, while the one centered at ≈ −0.16 eV to the antibonding e_g^π states. Fermi energy is set to zero.

An account of the SOC in the magnetic GGA+SOC calculations strongly changes the situation. It reduces the total moment, $\mu_z^{GGA+SOC} \sim 0.8\mu_B$/dimer, which is much smaller than in GGA, where $\mu_z^{GGA} \sim 2\mu_B$/dimer, and which is now consistent with the experimental value. This suggests the importance of the SOC. However, the SOC does not simply reduce the total moment due to direct contribution of orbital moment, which is expected to be antiparallel to spin, see Tab. I. This effect, commonly used for the description of the spin singlet state of Ir^{5+} ion (which for isolated ion could give nonmagnetic state[4–6]), leads in $Ba_5AlIr_2O_{11}$ to a decrease of the total moment only by ∼0.2 μ_B/dimer. Thus the observed reduction of the total moment of a dimer is not caused by the formation of $J = 0$ state on Ir^{5+}. This is due to the fact that we are dealing not with the isolated ions, but with a dimer, with significant hopping between sites

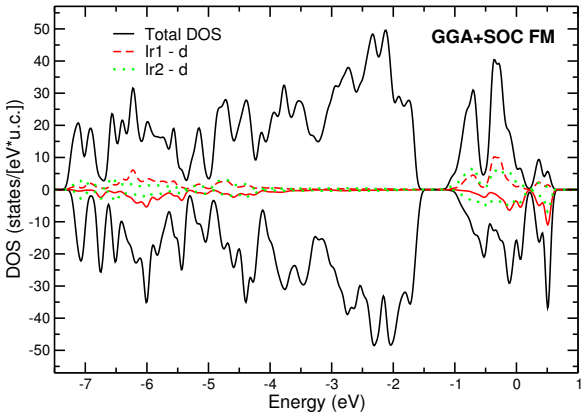

FIG. 4: (color online). Results of the ferromagnetic GGA+SOC calculations. Positive (negative) values correspond to spin majority (minority). Fermi energy is set to zero.

and with the average mixed valence of $Ir^{4.5+}$. It is clearly seen from Fig. 4, that the $5d$ orbitals of Ir1 and Ir2 are strongly hybridized and cannot be considered as ionic. The main reason for the reduction of the total moment is related to strong changes in the electronic structure and to breaking of the delicate balance between DE and SO states by the SOC.

These changes are easier to see in the nonmagnetic GGA+SOC calculations. One may notice in upper panel of Fig. 3 that the SOC basically shifts part of the antibonding MO to higher energy, due to formation of $j_{eff} = 1/2$ and $j_{eff} = 3/2$ subbands. The DOS center of gravity calculations shows that the splitting due to SOC is $\Delta_{SOC} \sim 0.6$ eV. This, together with the bonding-antibonding splitting is already sufficient to overcome the Hund's rule coupling and to suppress DE. Indeed, it is clearly seen in Fig. 4 that the SOC does not spoil main feature of the GGA band structure – the presence of bonding-antibonding splitting, but additionally lifts one of the antibonding orbitals up so that in effect $\Delta_{ae} + \Delta_{SOC} > J_H/2$, cf. Eq (2). Thus, the SOC plays on the side of covalency against DE. It also decreases the moment in the interstitial region down to 0.27 μ_B and mixes spin up and down states reducing spin moments on Ir sites, as shown in Tab. I. On the other hand the SOC does not act against charge disproportionation, which is given by the lattice distortions: $\delta n_{Ir1/Ir2}$ stays ∼0.3 electrons in the GGA+SOC calculations.

These theoretical results are consistent with experiment. Particularly, considerable weakened μ_{eff} is a result of common action of the SOC and covalency. As mentioned above, Ir ions forming dimer should not be considered as isolated ions, but they rather represent a single quantum-mechanical object having, due to joint effect of the SOC and covalency, strongly reduced magnetic moments. These moments can be coupled between dimers antiferromagnetically as usually occurs in insulating TM oxides[5]. This agrees with the low temperature of the magnetic transition and with negative θ_{CW}. It is important to note that small moment is experimentally seen already at temperatures much higher than the temperature of charge ordering; therefore it is not related with the formation of Ir^{4+} and Ir^{5+} ions (and correspondingly with $J = 0$ physics), but is rather explained by the competition between (covalency +SOC) and the Hund's exchange.

TABLE I: Magnetic moments obtained in the GGA+SOC calculations.

Ion	Spin moment, μ_B	Orbital moment, μ_B	μ_j(Ir), μ_B
Ir1 (Ir^{5+})	(0.02, 0.00, 0.53)	(-0.08, 0.00, -0.09)	0.44
Ir2 (Ir^{4+})	(0.09, 0.00, 0.24)	(-0.01, 0.00, -0.11)	0.15

In the end we would like to comment on the importance of the strong Coulomb correlations in $Ba_5AlIr_2O_{11}$. It is known that the correlation effects have to be take into account for correct description of the electronic and magnetic properties of various transition metal oxides[5,26]. We used GGA+U+SOC method to check how strongly the results of the DFT calculations depend on the Hubbard U[2732]. Typical values of U used in the literature for Ir ions changes from 1 to 1.5 eV, while Hund's intra-atomic exchange J_H is ~ 0.5 eV[8,28–30]. An account of on-site correlation effects usually lead to increase of the electron localization and growth of the spin moment, but the question is whether Hubbard U can overcome joint efforts of the SOC and strong covalency resulting in the formation of the metal-metal bonds and make one Ir^{4+} ($\mu_s = 1\mu_B$) and another Ir^{5+} ($\mu_s = 2\mu_B$). The results of the GGA+U+SOC calculations for $U = 1$ and 1.5 eV are shown in Tab. II. One may see, that while an account Hubbard correlations does lead to increase of the magnetic moments it is far from been so strong to overwhelm the SOC and the covalency.

Conclusions.– To sum up, with the use of the *ab initio* calculations we show in the present paper that it is the combined action of the spin orbit coupling and strong covalency which leads to suppression of magnetic moment in $Ba_5AlIr_2O_{11}$. Formation of the metal-metal bonds (covalency) alone is here not strong enough to suppress double exchange, which would favour the state with maximum spin. The spin-orbit coupling alone also would not be able to efficiently suppress magnetic moments on Ir, due to not complete Ir^{4+}/Ir^{5+} charge-ordering apparently caused by strong intersite electron hopping. Only combined action of both these mechanisms leads to the state with properties observed experimentally. We suppose that similar situation may also be met in other $4d$ and $5d$ transition metal compounds, e.g. in $Ba_3LnIr_2O_9$[31], where Ln is lanthanide.

Acknowledgments.– SS is grateful to Dr. Kateryna Foyevtsova for useful discussions. This work was sup-

TABLE II: Magnetic moments obtained in the GGA+U+SOC calculations.

Ion	Spin moment, μ_B	Orbital moment, μ_B	μ_j(Ir), μ_B
$U = 1$ eV			
Ir1 (Ir^{5+})	(0.02, 0.00, 0.64)	(-0.06, 0.00, -0.07)	0.56
Ir2 (Ir^{4+})	(0.07, 0.00, 0.35)	(-0.02, 0.00, -0.06)	0.29
$U = 1.5$ eV			
Ir1 (Ir^{5+})	(0.01, 0.00, 0.69)	(-0.05 0.00 -0.03)	0.66
Ir2 (Ir^{4+})	(0.05, 0.00, 0.42)	(-0.03 0.00 -0.01)	0.40

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* Electronic address: streltsov@imp.uran.ru

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[32] The "U-part" was taken as described in Ref.[27]. We also checked that a simplified version of the GGA+U, so called Dudarev's approach, with a single parameter $U_{eff} = U - J_H$ does not change the results of the calculations. E.g. for $U = 1.5$ eV, $J_H = 0.5$ eV ($U_{eff} = 1.0$ eV) Dudarev's approach gives $m_s^z(Ir1) = 0.68\mu_B$.